

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### NO DRAWINGS

#### Concrete Based Upon Epoxy Resins and Method of Making the Same

We, RELIANCE STEEL PRODUCTS COMPANY, a corporation of the State of Pennsylvania, having its principal place of business at 3700 Walnut Street, McKeesport, County of Allegheny, State of Pennsylvania, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for a composition of matter in the nature of concrete and for a method of preparing the same.

One object of this invention is to provide a material which has advantages as compared to conventional concrete.

According to this invention therefore there is provided a method of making concrete comprising the step of intermixing aggregate with a binder comprising an activator, a conventional epoxy resin derived from reacting epichlorohydrin and bisphenol and a catalyst comprising diethylene-triamine and diphenylguanidine.

In both military operations and civilian undertakings, there is need for a high early strength concrete. Many military operations might be facilitated with a suitable material, or even be possible only because of its availability. Many highway projects are delayed because of the inconvenience or congestion caused by the time required for concrete to cure in the making of alterations or repairs, and working time is often lost and equipment tied up on construction contracts between the pouring of concrete and waiting for it to harden. Even in such matters as repairing badly eroded highway surfaces where large areas of concrete are broken out, makeshift repairs must be resorted to because of the time element involved in using concrete where it should be used, but

where, because of the curing time, it is impractical to do so.

The compressive strength of concrete made with hydraulic cement is of the order of 3,000 pounds per square inch, and the maximum strength is reached about 28 days after the concrete is poured. Its strength in tension is negligible. So-called high early strength hydraulic concrete has about the same compressive strength, and its maximum strength for practical purposes is approached gradually and is reached after about 3 days.

In certain preparations according to the present invention, the concrete may have a compressive strength better than 20,000 pounds per square inch, with at least 90% of that strength being reached within 3 hours, and its final strength, for all practical purposes, being achieved in 5 or 6 hours. In addition, its tensile strength is of the order of several thousand pounds per square inch, and may be as high as 5,000 pounds per square inch.

In the repairing of concrete highways that have extensive areas broken out, and which may be cracked or in otherwise poor condition, conventional patching or surfacing materials often have a lower strength than the concrete itself, so that while a good appearing surface may be initially provided, the dead weight of the highway or bridge floor is increased, but the added material contributes little to the strength of the slab, so that the repaired surface soon starts to buckle or break away and fails to provide service commensurate with the cost.

Not only does a preferred embodiment of the invention provide a high early strength concrete, and one which has high tensile strength, but its modulus of elasticity in compression is higher than that of conventional concrete, and it is more shock-re-

sistant.

It can be laid over concrete and will adhere to it. Prepared as slabs, its compressive strength will exceed that of conventional pre-stressed concrete. It can, in a bridge floor, for example, be used in a slab of less thickness to secure the same load-carrying strength as conventional concrete, and thereby reduce the dead weight of the bridge floor. With reinforcing, it requires less steel, or no steel, for the same strength. Furthermore, it is non-porous and its water absorption is nil and its coefficient of thermal expansion is comparable to that of steel. Used over concrete paving for repair, it provides strength to it, relieving stress in the base and its reinforcing. A further object of the invention is to provide a concrete which may be formulated to meet specific requirements; its coefficient of thermal expansion can be closely matched to that of conventional concrete; its modulus of elasticity can be varied, and its compressive strength can be altered from its maximum downward, as conditions may require.

In order that the invention may be more readily understood, various preparations according to the present invention will now be described.

In the practice of our invention we prepare a resinous liquid binder which is mixed with aggregate preferably a specially prepared aggregate, which mixture is then poured or spread as any concrete.

The base resin of the liquid binder is a conventional type of epoxy resin produced by the reaction of bisphenol and epichlorohydrin. Such a resin is a light coloured syrup having an epoxide equivalent in the range of about 140-195, an average molecular weight of the order of 300-400, a viscosity at 25°C. of 5000 to 16,000 centipoises, and a colour at 25°C. of 5-8 Gardner. The products of different manufacturers vary in these properties, but typical resins useful as the base ingredient are sold by Ciba Chemical Corporation under the Trade Mark 'Epoxy 6010' and by Shell Chemical Corporation under the designation "Epon 828".

With the resin are combined one or more activators, two such activators being employed to give maximum utility to the invention where high early strength curing is desired, but either one of which could be used alone where the maximum benefits are not required.

The first activator, which may be referred to as formulation No. 1, is a highly reactive epoxy resin which has also the property of lowering the viscosity of the base resin, the resin preferably having phenol dissolved therein. This solution acts to substantially accelerate the curing of the resin or activate its functioning. The fast reacting epoxy resin here used is conveniently the reaction pro-

duct of epichlorohydrin and glycerol, an aliphatic compound as contrasted with bisphenol which is an aromatic compound. One commercially available resin which may be used is sold by Shell Chemical Corporation under the designation "Epon 812", and is more fully described in the technical bulletin published by that company, SC 58-92. It is the fastest reacting of the commercial epoxy resins and it and other similar highly reactive epoxy resins will be herein designated "fast-reacting epoxy resin" to distinguish from the conventional base epoxy resin above described. Phenol is readily dissolved in this fast reacting resin, and for convenience the phenol and fast-reacting resin are combined to provide one activator before preparation of the final mix.

The second activator is triphenyl phosphite. It is commercially available under the trade-mark "Mod-epox", and is a product of Monsanto Chemical Corporation.

The binder comprising the base resin and preferably the two activators preferably has mixed therewith a diluent or extender which may or may not be reactive with the other ingredients. A non-reactive extender is liquid road oil. A grade designated generally as "R T 5" in the paving industry is the most satisfactory, although liquid grades of a similar character may be used. (Road oil is classified from 1 to 12 according to viscosity, grade RT12 having a high coefficient of viscosity and grade R T 5 being of medium viscosity.)

In lieu of R T 5, which is a non-volatile tar byproduct of the coking of coal, or as a partial replacement thereof, we may use a low viscosity liquid low molecular weight polyamide resin. Polyamide resin sold by General Mills Inc. under the Trade Mark "Versamid 140" is such a resin and for the sake of convenience it will be referred to hereinafter as "Versamid 140". It renders the base mix more fluid, acting to lower its viscosity. Unlike road oil, it enters into the system or co-polymerizes with the epoxy resin and serves to flexibilize the cured mass.

The final ingredient of the liquid mix is the catalyst or curing agent. It is a mixture of diethylene triamine (DETA) and diphenylguanidine (D.P.G.) and may be termed formulation No. 2.

The fast-reacting epoxy resin of formulation No. 1 functions to reduce the viscosity of the final mix and is a rapid curing resin. In the cured mass it acts as an internal plasticizing ingredient and also improves the impact strength of the mass.

Phenol dissolved in the fast-reacting epoxy resin is an activator for the amine catalyst. It gives a very fast initial gel time to the mix and is important in bringing

about rapid load bearing strength.

If rapid initial gel and early high strength are not required, phenol may be omitted and the fast-reacting resin used alone. The fast-reacting resin could be replaced entirely by phenol if the plasticizing property and fast initial gel are not important.

The triphenyl phosphite is a reactive diluent in the mixture and is important to the system in giving it dimensional stability under heavy loads and giving the mass a higher ultimate compressive strength. It may perhaps be expressed as imparting the property of good elastic quality, but resisting plastic flow. Also, in the mix, it acts to accelerate the action of the amine curing agent or catalyst.

Triphenyl phosphite could theoretically replace the first activator entirely; that is, the fast-reacting epoxy resin and phenol solution, if early gel strength and extremely fast curing and early strength are not required.

DETA is of course a commonly used curing agent or catalyst for epoxy resin, but used alone its action is relatively slow. On the other hand, D.P.G. used alone will react with the base epoxy resin with almost explosive violence. The D.P.G. functions the same as an amine catalyst but used alone is too reactive. Mixed with DETA it triggers the hardening process. It, too, is an accelerator, but primarily to accelerate initial curing, as distinguished from the two activators which accelerate curing after the initial reaction has been triggered.

The first activator, Formulation No. 1, preferably comprises:

66 2/3% fast-reacting epoxy resin, and  
33 1/3% phenol  
Total 100%

These proportions may, however, vary between

20 to 80% of the resin, and  
80 to 20% of phenol  
Total 100%

The catalyst formulation, which may be referred to as Formulation No. 2 is preferably comprised of

DETA 95%  
D.P.G. 5%  
Total 100%

These ingredients may vary, however, in about the following range:

DETA 80 to 95%  
D.P.G. 5 to 20%  
Total 100%

A preferred total liquid binder system has the following formulation:

**Example 1**

Ingredients	Parts by Weight
Base epoxy resin	— 57
Formulation 1 above	— 5
Triphenyl phosphite	— 5
Road Oil — R T 5	— 27

Curing agent — Formulation 2 above

— 6  
Total 100

Formulations may be prepared, however, within the following limits:

**Example 2**

Ingredients	Parts by Weight
Base epoxy resin	— 35 to 75
Formulation 1 above	— 3.5 to 7.5
Triphenyl phosphite	— 3.5 to 7.5
Road Oil — R T 5	— 53 to 0
Curing agent — Formulation 2 above	— 5 to 10
Total	100

An example using "Veramid 140" or similar low-molecular weight liquid low viscosity polyamid resin in addition to R T 5 comprises:

**Example 3**

Ingredients	Parts by Weight
Base epoxy resin	— 40.6
Formulation 1 above	— 3.6
Triphenyl phosphite	— 3.6
Road Oil — R T 5	— 26.6
Versamid 140	— 21.4
Curing agent — Formulation 2 above	— 4.2
Total	100

From the foregoing it will be seen that the base epoxy resin or conventional resin is the predominant ingredient of the binder, but that the extender and flexibilizing agent are preferably in a range of roughly 50% of the weight of the total epoxy resin content to about an equal weight therewith. Formulations 1 and 2, which comprise activators and catalysts or curing agents for the base resin, preferably do not exceed 12% of the total weight of the liquid mix, nor do they comprise substantially less than 8%, and the fast-acting resin is here included as an activator. Substantially lesser amounts slow down the curing unless temperatures are high and substantially greater amounts accomplish no improvement in the rate of curing, and may even interfere with proper curing, or be detrimental to the finished product.

According to a further example, the binder may comprise 35 to 75 parts by weight of a conventional epoxy resin produced from the reaction of epichlorohydrin and bisphenol 3.5 to 7.5 parts by weight of a solution made up of 20% to 80% by weight of fast-reacting epoxy resin and 80% to 20% by weight of phenol; 3.5 to 7.5 parts by weight of triphenyl phosphite; approximately 26.6 parts by weight of road oil of medium viscosity such as the grade RT5; approximately 21.4 parts by weight of a low-viscosity low molecular weight polyamide resin; and 5 to 10 parts by weight of a catalyst comprising 80% to 95% by weight of diethylenetriamine and 5% to 20% by weight of diphenylguanidine, the

total number of parts by weight in the combined mixture being 100, and the concrete may comprise approximately 10 parts by weight of binder to 90 parts by weight of high density low void aggregate.

All of the ingredients used together are miscible and do not segregate, although there may be some which, in the absence of another, would not be miscible or mutually soluble.

For high early strength applications, the aggregate should be carefully selected. A high-density minimum void aggregate is especially useful for this purpose and may comprise:—

	Ingredients	Parts by Weight
	3/8" washed gravel	— 10%
	Grits	— 40%
20	Concrete Sand	— 20%
	Masonry Sand	— 30%
	Total	— 100%

This aggregate weighs approximately 107 lbs. per cubic foot loose weight and has an average of 35% voids, and is a typical high-density minimum void aggregate well known in the concrete art.

About 10% by weight of the liquid system is mixed with about 90% by weight of such a high-density minimum void aggregate for optimum results.

The aggregate is thoroughly dried before it is used. Preferably it is heat-dried and mixed with the liquid binder while still warm, especially when ambient temperatures are below 70°F. After the mix has been prepared, it is immediately poured or poured and spread and the resin allowed to cure *in situ*.

A mix formulated with the preferred binder composition develops strength in compression in three hours in excess of 3000 lbs. per square inch and therefore meets or exceeds usual Highway Department or other strength specifications for fully-cured concrete. Hence after material is put down and spread on a road, it may be opened to traffic in three hours, or if used in a structure, it is ready for use in that time.

With 10% binder the concrete has a coefficient of thermal expansion of  $8 \times 10^{-6}$  inch per inch per degree Fahrenheit.

With 11% binder the coefficient of thermal expansion is  $10 \times 10^{-6}$  inch per inch per degree Fahrenheit.

The corresponding figures for normal concrete is 6 to  $7 \times 10^{-6}$  inch, so that the cured concrete of this invention closely matches that of fully-cured hydraulic concrete.

Notwithstanding its high compressive strength, it is sufficiently flexible or elastic without plastic flow to be compatible with concrete. It bonds to the concrete more strongly than conventional hydraulic con-

crete coheres.

The concrete may be used for almost any construction work where conventional concrete is required. While the cost per cubic yard may exceed that for hydraulic cement concrete, the fact that it has greater strength and can be used in thinner slabs or smaller columns, plus the saving of time or labour and stand-by time for equipment and work crews offset completely, or to a large measure, the greater material cost. If the dead load of bridge floor can be substantially reduced, as this invention permits, the steel in the bridge itself may be lighter, or an old bridge can be lightened to carry greater live loads. Militarily, a bomb or fall-out shelter can be quickly produced, or an air strip prepared or repaired in a matter of hours. Roads may be repaired by extensive resurfacing overnight, and be ready for use the following morning. Used over existing concrete, it will bond to existing surfaces and may be applied no thicker than asphalt is generally applied, but with much more permanent results. Where ambient temperatures are much below 70°F., the aggregate should be moderately heated at the time the batch is prepared, and artificial heat may be supplied. Because of its high strength it will reinforce and strengthen concrete road surfaces to which it is applied even though the concrete is old, weathered, eroded, and has large areas broken out, or the concrete cracked.

Properties of the concrete may be varied to suit conditions. Generally an increase in the resin-to-aggregate ratio will produce a concrete having a greater coefficient of thermal expansion. Where higher tensile strength is required, stronger aggregate may be used. For example, aluminium oxide aggregate adds strength. The modulus of elasticity can be varied by adding, omitting, or reducing the extender or elasticizing medium or media.

#### WHAT WE CLAIM IS:—

1. A method of making concrete comprising the step of intermixing aggregate with a binder comprising an activator, a conventional epoxy resin derived from reacting epichlorohydrin and bisphenol, and a catalyst comprising diethylenetriamine and diphenylguanidine.

2. A method of making concrete according to claim 1 wherein the activator is a fast reacting epoxy resin.

3. A method of making concrete according to claim 1 wherein the activator comprises a fast reacting epoxy resin and phenol.

4. A method of making concrete according to claim 3 wherein phenol and the fast reacting epoxy resin are in the ratio of 20 to 80 parts by weight of fast reacting epoxy resin, to 80-20 parts by weight of phenol,

and there is one part by weight of phenol and fast reacting epoxy resin to approximately 9 to 10 parts by weight of the conventional epoxy resin.

5 5. A method of making concrete according to claim 1 wherein the said activator is triphenyl phosphite.

6. A method of making concrete according to claim 1 wherein the said activator comprises fast reacting epoxy resin, phenol, 10 and triphenyl phosphite.

7. A method of making concrete comprising the step of intermixing aggregate with a binder comprising, a conventional 15 epoxy resin derived from reacting epichlorohydrin and bisphenol, a catalyst comprising diethylenetriamine and diphenylguanidine, and an activator including a fast reacting epoxy resin, phenol, or a mixture thereof.

20 8. A method of making concrete according to any one of the preceding claims wherein the said binder includes an extender or diluent.

9. A method of making concrete according to claim 8 wherein the said extender or 25 diluent is road oil.

10. A method of making concrete according to claim 8 wherein the extender or diluent comprises road oil and a low 30 molecular weight polyamide resin.

11. A method of making concrete according to any one of the preceding claims wherein the catalyst comprises 80% to 95% by weight diethylenetriamine, and 5% to 35 20% by weight diphenylguanidine.

12. A method of making concrete according to any one of the preceding claims wherein the catalyst comprises approximately 95% by weight diethylenetriamine and 5% 40 by weight diphenylguanidine.

13. A method of making concrete substantially as hereinbefore described with reference to Example 1.

14. A method of making concrete substantially as hereinbefore described with reference to Example 2. 45

15. A method of making concrete substantially as hereinbefore described with reference to Example 3.

50 16. A method of making concrete

according to claim 1 wherein the binder comprises 35 to 75 parts by weight of conventional epoxy resin produced from the reaction of epichlorohydrin and bisphenol; 3.5 to 7.5 parts by weight of a solution 55 made up of 20% to 80% by weight of fast reacting epoxy resin and 80 to 20% by weight of phenol; 3.5 to 7.5 parts by weight of triphenyl phosphite; approximately 26.6 parts by weight of road oil of medium viscosity such as the grade RT5; approximately 21.4 parts by weight of a low-viscosity low molecular weight polyamide resin; and 5 to 10 parts by weight of a catalyst comprising 80% to 95% by weight of diethylenetriamine and 5% to 20% by weight of diphenylguanidine, the total number of parts by weight in the combined mixture being 100, and wherein the concrete comprises approximately 10 parts by weight of 70 binder and 90 parts by weight of high density low void aggregate.

17. A method of making concrete according to any one of the preceding claims wherein the aggregate is of high density 75 with comparatively few voids.

18. A method of making concrete according to any one of the preceding claims wherein the aggregate is heat dried and is warmer than the ambient temperature at 80 the time of mixing.

19. A method of making concrete according to any one of the preceding claims, wherein the activator includes a fast reacting epoxy resin which is the product 85 of reacting epichlorohydrin and glycerol.

20. Concrete prepared by a method according to any one of the preceding claims.

21. The binder used in the concrete 90 according to claim 20.

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